

Investigation of Structure and Transport in Li-doped Ionic Liquid Electrolytes: [pyr14][TFSI], [pyr13][FSI] and [EMIM][BF₄]

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Ionic liquid electrolytes have been proposed as a means of improving the safety and cycling behavior of advanced lithium batteries; however, the properties of these electrolytes under high lithium doping are poorly understood. Here, we employ both polarizable molecular dynamics simulation and experiment to investigate the structure, thermodynamics and transport of three potential electrolytes, N-methyl-N-butylpyrrolidinium bis(trifluoromethylsulfonyl)imide ([pyr14][TFSI]), N-methyl-N-propylpyrrolidinium bis(fluorosulfonyl)imide ([pyr13][FSI]), and 1-ethyl-3-methylimidazolium boron tetrafluoride ([EMIM][BF₄]), as a function of Li-salt concentration and temperature. Structurally, Li⁺ is shown to be solvated by three anion neighbors in [pyr14][TFSI] and four anion neighbors in both [pyr13][FSI] and [EMIM][BF₄], and at all levels of x_{Li} we find the presence of lithium aggregates. Furthermore, the computed density, diffusion, viscosity, and ionic conductivity show excellent agreement with experimental data. While the diffusion and viscosity exhibit a systematic decrease and increase, respectively, with increasing x_{Li} , the contribution of Li⁺ to ionic conductivity increases until reaching a saturation doping level of $x_{\text{Li}} \sim 0.10$. Comparatively, the Li⁺ conductivity of [pyr14][TFSI] is an order of magnitude lower than that of the other liquids, which range between 0.1-0.3 mS/cm. The differences in Li⁺ transport are reflected in the residence times of Li⁺ with the anions, which are revealed to be much larger for [pyr14][TFSI] (up to 100 ns at the highest doping levels) than in either [EMIM][BF₄] or [pyr13][FSI]. Finally, we comment on the relative kinetics of Li⁺ transport in each liquid and we present strong evidence for transport through anion exchange (hopping) as opposed to the net motion of Li⁺ with its solvation shell (vehicular).